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# A simple model for diffusion-induced dislocations during the lithiation of crystalline materials

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**Abstract** Assuming that the lithiation reaction occurs randomly in individual small particles in the vicinity of the reaction front, a simple model of diffusion-induced dislocations was developed. The diffusion-induced dislocations are controlled by the misfit strain created by the diffusion of solute atoms or the phase transformation in the vicinity of the reaction front. The dislocation density is proportional to the total surface area of the "lithiated particle" and inversely proportional to the particle volume. The diffusion-induced dislocations relieve the diffusion-induced stresses.

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**Keywords** diffusion, misfit strain, dislocation density, lithiation

In studying the stress evolution in Si due to solute lattice contraction of B and P, Prussin[1] observed the generation of dislocations in Si wafers and proposed that the dislocation density is proportional to the derivative of the solute concentration with respect to spatial variable. Huang et al.[2] performed in-situ observation of electrochemical lithiation of a $SnO_2$ nanowire inside a transmission electron microscope and observed that there exist mobile dislocations of a high density associated with the reaction front. They suggested that the high density of mobile dislocations reveals large misfit stresses and is the driving force for solid-state amorphization. However, they did not analyze the generation of dislocations.

It is known that the lithiation and delithiation in lithium-ion battery (LIB) can lead to the volume change of Sn and Si during electrochemical charging and discharging.[3] In studying the stress evolution during electrochemical cycling, the current research approach used in the community of LIBs has strongly relied on diffusion-induced stress,[4–8] which is based on the theory of linear elasticity.[9] In commenting on the recent work by Wei et al.,[10] Yang[11] related the dislocation density tensor to the diffusion-induced strain by following the work of Indenbom[12] for thermoelastic strains, and proposed a relationship between the change of plastic strain and the concentration of solution atoms. He did not consider the effect of misfit strains (stresses) on the generation of dislocations. In this work, a simple model of dislocation generation due to the diffusion-induced misfit strain is proposed. The dependence of dislocation density on the misfit strain is discussed.

The diffusion of solute atoms can lead to elastoplastic deformation, and the generation of dislocations can relieve the diffusion-induced stresses in materials. During lithiation, the material at the lithiated state experiences volumetric expansion, which introduces misfit strains between

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the lithiated material and the unlithiated material. Assume that the lithiation reaction occurs randomly in individual small particles in the vicinity of the reaction front (as shown in Fig. 1) instead of over the whole reaction front. For simplicity, the particle is assumed to be rectangular prism. The misfit strain $\varepsilon_{\text{misfit}}$, created by the phase transformation or the diffusion of solute atoms, can be expressed as $\varepsilon_{\text{misfit}} = \Delta l_i / l_i = \Omega c/3$ for isotropic materials. Here, $l_i$ $(i = 1, 2, 3)$ are the side lengths of the particle, $\Omega$ is the coefficient of the volume change per mole of solute atoms, and $c$ is the concentration of solute atoms. Large misfit strain can cause plastic deformation in the material near the reaction front and lead to emission of dislocations to relieve the mechanical stresses. Assume that the dislocation generation is controlled by the emission of dislocation loops. According to the Orowan relation,[13] the total number of dislocations emitted in the $i$-th direction, $N_i$, can be calculated as

$$N_i = \varepsilon_{\text{misfit}}/b = \alpha_i \Omega c/(3b). \tag{1}$$

Here, $b$ is the magnitude of Burgers vector, $\alpha_i$ represents the contribution from the deformation in the $i$-th direction and is related to the average displacement of the dislocation loops in the $i$-th direction. For isotropic materials, $\alpha_i$ is a function of the mechanical properties of the lithiated material and the unlithiated material and the size of the particle in the $i$-th direction, which can be approximated as $l_i$ if there are no dislocation-dislocation and dislocation-interface (reaction front) interactions.

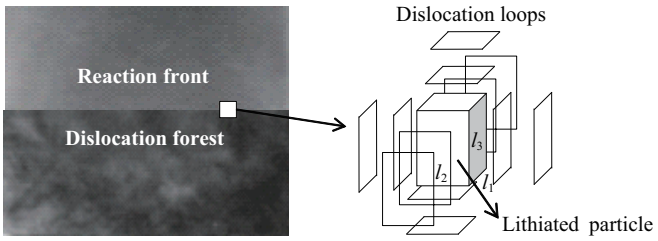


Fig. 1. Schematic of the emission of dislocation loops from a lithiated particle in the vicinity of the reaction front during electrochemical charging.

It is reasonable to assume that the dislocation loops emitted have the geometrical shape approximately the same as the cross-section of the particle in the corresponding direction. Using Eq. (1), one can calculate the total length of the dislocations emitted from the particle as

$$\begin{aligned} L \approx 2\left[N_1(l_2+l_3)+N_2(l_1+l_3)+N_3(l_1+l_2)\right] = \\ 2\Omega c\left[l_1(l_2+l_3)+l_2(l_1+l_3)+l_3(l_1+l_2)\right]/(3b). \end{aligned} \tag{2}$$

Under the condition that the dislocation back stresses and the dislocation-interface (reaction front) interaction are negligible, the number of the particles in a unit volume in the vicinity of the reaction front can be estimated as

$$n = f/(l_1 l_2 l_3), \tag{3}$$

where $f$ is the volume fraction of the reaction particles in the vicinity of the reaction front. Sub-

stituting Eq. (3) in Eq. (2), one obtains the total length of the dislocations emitted in the vicinity of the reaction front as $L_{\text{total}} \approx nL = 4\Omega cf(1/l_1 + 1/l_2 + 1/l_3)/(3b)$ and the dislocation density behind the reaction front as $\rho = L_{\text{total}}/(1-f) = [f/(1-f)][4\Omega c/(3b)](1/l_1 + 1/l_2 + 1/l_3)$. The dislocation density is proportional to the local concentration of solute atoms, as expected, and the summation of the inverse of $l_i$. For a rectangular prism, the ratio of the total surface area $A$ to the volume $V$ is $A/V = 2(1/l_1 + 1/l_2 + 1/l_3)$ which gives

$$\rho = [f/(1-f)][2\Omega c/(3b)](A/V). \tag{4}$$

The dislocation density is proportional to the total surface of the "lithiated particle" and inversely proportional to the particle volume. For the same $f$ of "lithiated particles", the smaller the "lithiated particles" the higher a dislocation density will be created.

To examine the shape effect, we consider two geometrical shapes of the "lithiated particles" with cube ($l_1 = l_2 = l_3$) and platelet ($l_1 = l_2 = 10l_3$) having the same volume fraction. Figure 2 shows the variation of the dislocation density with $\sqrt{l_1 l_2}$. Obviously, the "lithiated particles" of the platelet shape produces a higher dislocation density for the same base area of $l_1 l_2$.

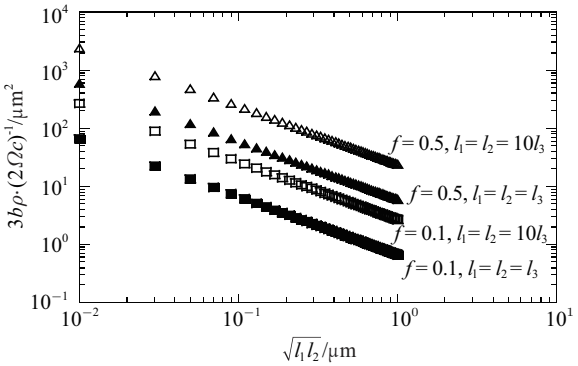


Fig. 2. Calculated dislocation density due to the diffusion-induced dislocations as a function of the square root of the base area.

In general, Eq. (4) can be extended to the "lithiated particles" of other shapes and can be written as $\rho = [f/(1-f)][\chi\Omega c/(3b)](A/V)$, with $\chi$ being a function of the geometry of the "lithiated particles". Once the dislocation density is determined, the strain field can be obtained. For a dislocation loop $C$, the strain components are[14] $\varepsilon_{ij}^{\text{dis}} = [1/(8\pi)] \oint_C [-(1/2)(\in_{jkl} b_i R_{,l} + \in_{ikl} b_j R_{,l} - \in_{ikl} b_l R_{,j} - \in_{jkl} b_l R_{,i})_{,pp} + \in_{kmn} b_n R_{,mij}/(1-\nu)]\, \mathrm{d}C_k$, in which $b_i$ are the components of Burgers vector, $\in_{ijk}$ are the components of the permutation tensor, and $R = ||\boldsymbol{r} - \tilde{\boldsymbol{r}}||$. $\boldsymbol{r}$ is the position vector, and $\tilde{\boldsymbol{r}}$ is the position vector of a dislocation segment. The strain components created by $N$ $(N = N_1 + N_2 + N_3)$ dislocations can be calculated as

$$\varepsilon_{ij}^{\text{dis}} = \sum_{\kappa=1}^{N} [1/(8\pi)] \oint_{C^{(\kappa)}} \big[ -(1/2)\big( \in_{jkl} b_i^{(\kappa)} R_{,l}^{(\kappa)} + \in_{ikl} b_j^{(\kappa)} R_{,l}^{(\kappa)} - \in_{ikl} b_l^{(\kappa)} R_{,j}^{(\kappa)} - \in_{jkl} b_l^{(\kappa)} R_{,i}^{(\kappa)} \big)_{,pp} + \in_{kmn} b_n^{(\kappa)} R_{,mij}^{(\kappa)}/(1-\nu) \big]\, \mathrm{d}C_k^{(\kappa)}. \tag{5}$$

Using Eq. (5), the constitutive relationship describing the stress in the lithiated material can be

expressed as

$$\sigma_{ij} = C_{ijkl}(\varepsilon_{kl} - \varepsilon_{kl}^{\text{dis}}). \tag{6}$$

Here $\sigma_{ij}$ are the components of stress tensor, $C_{ijkl}$ are the components of the fourth-order tensor of linear elastic moduli, and $\varepsilon_{ij}$ are the components of strain tensor. The equilibrium equation in the vicinity of the reaction front is

$$\sigma_{ij,j} = 0. \tag{7}$$

Equations (6) and (7) provide the base for analyzing the stress evolution during electrochemical charging and discharging in LIBs.

In summary, a simple model was developed for the diffusion-induced dislocations for the lithiation of crystalline materials in lithium-ion battery. Assuming that the dislocation back stresses and the interaction between dislocations and the reaction front are negligible, the dislocation density is proportional to the total surface area of the "lithiated particle" and inversely proportional to the particle volume. For the same volume fraction of lithiated particles in the vicinity of the reaction front, the smaller the lithiated particles the higher a dislocation density will be created. The diffusion-induced dislocations relieve the diffusion-induced stresses. One needs to consider the contribution of the diffusion-induced dislocations in analyzing the stress field in crystalline materials during electrochemical charging and discharging.


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